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FROM  
PINE GUM

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A New Product for Industry

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## PREFACE

The principal purpose of this publication is to apprise industry of opportunities for profitable new commercial ventures arising from research conducted by USDA's Agricultural Research Service on naval stores products. In addition, it provides a medium through which the Southern Utilization Research and Development Division can better serve the naval stores industry and, in return, receive practical guidance for future research designed to benefit agriculture, processors, and the consumer.



# PEROXIDES FROM PINE GUM

A New Product for Industry

by

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## INTRODUCTION

The demand for rosin has been gradually diminishing because of advances in the production of synthetic detergents and new paper finishing agents. A potential outlet for over 5,000,000 pounds a year of new peroxidic products derived from oleoresin--generally called pine gum--is envisioned based on research studies conducted by the Southern Utilization Research and Development Division. A simple, low-cost process for the production of inexpensive peroxidic products by the oxidation of pine gum presents the naval stores industry with an opportunity to increase markets and to improve sales profits.

The product, a free-flowing solid, consists primarily of a mixture of three peroxides

obtained from the major acids of the gum with an active oxygen content of approximately three percent. As a source of active oxygen the gum peroxides will successfully compete for the markets being held by more costly peroxides. Under certain conditions, potentially useful diepoxides can be made from the acid peroxides.

Applications for the new materials, based on properties and preliminary evaluation studies, indicate utility as catalysts for polymerization reactions, as curing or vulcanizing agents, in casting and laminating resins used for the construction of boats and structural panels, and as agents to improve the properties of rubber.

### PROPERTIES

Name: Photosensitized-oxidized pine gum  
Formula: Essentially a mixture of levopimaric, palustic, and neoabietic acid peroxides

### Physical Properties

Appearance: Free-flowing, off-white solid  
Molecular Weight: 318 (average)  
Softening Point: 61-73°C.  
Solubility: Soluble in acetone, benzene, ether, alcohols; insoluble in water and isooctane

### Chemical Properties

The mixture of peroxides is stable to shock and can be struck with a hammer without detonating. It can be stored at room temperature for over nine months without decrease in peroxide content. Photosensitized-oxidized pine gum is sensitive to both strong acids and strong bases. The half life of the peroxide mixture at varying temperatures, in benzene, is as follows:

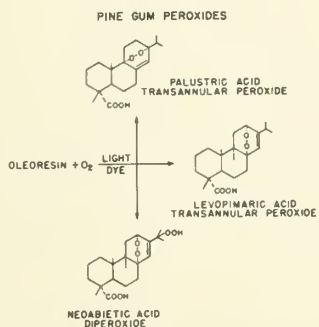


Figure 1. --Pine gum peroxides

Temperature, ° C.	Half Life, Minutes
190	1.6
155	12
140	49
125	106

## POSSIBLE USES OF PEROXIDE AND DIEPOXIDE

### Peroxides

- Initiators or catalysts in the synthesis of plastics and rubber
- Curing or vulcanizing agents
- Stabilizer for polyvinyl chloride
- Casting and laminating resins
- Polymerization of vinyl monomers
- Styrenated casting resins, polymerized gum rosin, polymerized ester gum, and other industrial products

### Rosin Diepoxide

- Adhesives
- Casting and laminating resin
- Surface coatings

## ECONOMICS

Without the benefit of detailed cost estimates, only general comments can be made regarding economics. Since pine gum sells at 8 cents a pound, and with only a minimal quantity of other inexpensive chemicals consumed in the operation, the final products can probably be made in moderate quantities at a cost of less than 25 cents a pound. Competitive products are currently selling from 75 cents to \$3 a pound.

Relatively simple and inexpensive equipment can be used for manufacturing the peroxides. Capital investment costs for the production of 2,000,000 pounds a year need not exceed \$500,000.

## TOXICITY

The toxicity of photosensitized-oxidized pine gum and rosin diepoxide is not known at the present time.

## SAMPLES

Samples of oxidized pine gum and the diepoxide can be obtained for test purposes by writing to the Naval Stores Laboratory, Olustee, Fla.

## ACCOMPLISHMENTS

The Southern Utilization Research and Development Division has developed a practical process for the production of useful peroxides from crude pine gum. Photosensitized oxidations of slash and longleaf pine gum, scrape and gum rosin were investigated. Because of its high levopimaric acid content pine gum was selected as a desirable starting material. Rose bengal is an efficient sensitizer for the oxidation reaction. Shelf life studies over a nine-month period indicated no loss of the peroxide content. The life of oxidized pine gum samples was determined.

It has also been shown that certain resin acid peroxides--for example, that obtained from levopimaric acid--will form a diepoxide when heated in an inert solvent.

## PROCESS

The laboratory procedure for the preparation of the peroxides consisted of placing approximately two liters of a 15 percent methanol solution of pine gum, to which was added approximately 0.1 percent of rose bengal, in the outer shell of a concentric reactor about four feet high and approximately 3 inches in diameter with an inner tube containing a 40-watt fluorescent light. The outer tube was provided with an air inlet through a sintered glass plate at the bottom. Four 15-watt fluorescent lights were arranged externally around the reactor with provisions for air cooling by circulation. Aeration at the rate of 5 to 10 cubic feet of air per hour, with all of the lights on and the temperature of the solution maintained at about 30°C., was continued for approximately 9 hours. The solution was then treated with 75 grams of Norit-A, filtered, and stripped under vacuo at a temperature of

about 60°C. to remove methanol and turpentine. The friable solid residue was crushed and air-dried, whereby an off-white free-flowing powder containing 3.12 percent active oxygen was obtained. The yield was essentially quantitative, based on the rosin content of the pine gum.

## MATERIALS AND EQUIPMENT

### Raw Materials

Pine gum  
Methanol  
Dye (rose bengal)  
Activated carbon (Norit-A)

### Equipment

For the production of a technical grade product, equipment constructed of mild carbon steel should prove to be adequate. To minimize metal contamination especially if the methanol solution of the pine gum is pretreated with carbon before aeration, it may be desirable to use glass lined or stainless steel reactors and finishing stills. More practicable for large scale production is a continuous system consisting of reactors jacketed for cooling and equipped with annular fluorescent lights set in long pyrex tubes, similar to reactors being used for continuous chlorination. A suggested flow diagram follows.

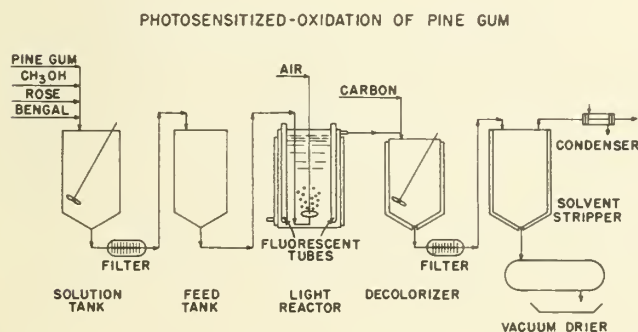


Figure 2. --Photosensitized-oxidation of pine gum.

## SCOPE OF INVESTIGATIONS

The rate of reaction in a photosensitized-oxidation is independent of temperature and pressure; for convenience, the reaction was carried out at room temperature and atmospheric pressure. However, the rate is directly proportional to the amount of light supplied to the system--the more intense the light, the faster the reaction. The quantity of pine gum in the solution can be increased to 75 percent solids, but the most convenient concentration is between 10 to 30 percent resin acid solids.

Mixed rosin diepoxides were prepared by refluxing a 20 percent solution of the oxidized gum in xylene for approximately one hour. The solvent was removed under reduced pressure to yield the rosin diepoxides as a residue.

## KEY PERSONNEL INVOLVED ON PROJECT

Naval Stores Laboratory, Olustee, Fla. <sup>1/</sup>

R. V. Lawrence  
W. H. Schuller  
R. N. Moore

## PUBLICATIONS AND PATENTS <sup>2/</sup>

### Publications

AIROXIDATION OF RESIN ACIDS. I. PHOTO-SENSITIZED OXIDATION OF LEVO-PIMARIC ACID. Moore, R. N.; and Lawrence, R. V. J. Am. Chem. Soc. 80(6): 1438-1440, 1958. (Reprint No. 1606)

PREPARATION OF 6-HYDROXYDEHYDROABIETIC ACID FROM THE PHOTO-PEROXIDE OF LEVOPIMARIC ACID. Moore, R. N.; and Lawrence, R. V. J. Am. Chem. Soc. 81, 458-460, 1959. (Reprint No. 1760)

STRUCTURE OF PALUSTRIC ACID. Schuller, W. H.; Moore, R. N.; and Lawrence, R. V. Chem. & Ind. (London) 954, 1959. (Reprint No. 1856)

<sup>1/</sup> One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.  
<sup>2/</sup> Reprints may be requested by reprint number.

AIR OXIDATION OF RESIN ACIDS. II. THE STRUCTURE OF PALUSTRIC ACID AND ITS PHOTSENSITIZED OXIDATION. Schuller, W. H.; Moore, R. N.; and Lawrence, R. V. J. Am. Chem. Soc. 82, 1734-1738, 1960. (Reprint No. 1932)

PHOTO-SENSITIZED OXIDATION OF A TRANS DIENE AND THE CONFIGURATIONS OF THE PINE GUM RESIN ACIDS. Schuller, W. H.; and Lawrence, R. V. Chem. & Ind. (London), 105-106, 1961. (Reprint No. 2073)

AIR OXIDATION OF RESIN ACIDS. III. THE PHOTSENSITIZED OXIDATION OF NEOABIETIC ACID AND THE CONFIGURATIONS OF THE PINE GUM RESIN ACIDS. Schuller, W. H.; and Lawrence, R. V. J. Am. Chem. Soc. 83, 2563-2570, 1961. (Reprint No. 2142)

PHOTSENSITIZED OXIDATION OF PINE GUM TO YIELD PEROXIDES. Schuller,

W. H.; Minor, J. C.; and Lawrence, R. V. Ind. Eng. Chem., Prod. Res. Develop. 3, 97-100, 1964. (Reprint No. 2732)

#### Patents

HYDROPEROXY-SUBSTITUTED ROSIN MATERIALS AND A METHOD FOR THEIR PRODUCTION. McKennon, F. L.; and Lawrence, R. V. U. S. Patent No. 2,653,922.

PREPARATION OF OXYGENATED RESIN ACID DERIVATIVES. Moore, R. N.; and Lawrence, R. V. U. S. Patent No. 2,889,463.

METHOD FOR PRODUCING PHOTO-PEROXIDES. Moore, R. N.; and Lawrence, R. V. U. S. Patent No. 2,996,515.

No patent warranties are hereby granted, implied, or otherwise made.